

Silica-coated poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing organic phase change materials

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Abstract

Macroporous sorbents differing in size were prepared by the 2,2'-azobis(isobutyronitrile) (AIBN)-initiated suspension radical polymerization of glycidyl methacrylate and ethylene dimethacrylate in the presence of an inert porogen. The microspheres were loaded with paraffin and cetyl alcohol phase change materials (PCMs) and coated with silica by sol-gel method using trimethoxy(methyl)silane hydrolysate. The energy storing capacity of the PCM-containing composite particles was monitored by differential scanning calorimetry. Accelerated thermal cycling tests were carried out to determine the thermal reliability of the microencapsulated PCMs. Paraffin and cetyl alcohol content in the microcapsules was 42.9 wt.% and 48.9 wt.%, respectively. The microcomposites with higher PCM content showed correspondingly higher latent heat storage capacity (melting and solidification enthalpies were 96.1 J/g and 94.5 J/g, respectively). However, there was low enthalpy change observed after 1000 thermal cycles of cetyl alcohol-containing capsules, which indicated that PCM leakage from the microspheres was minimal.

Keywords: porous poly(glycidyl methacrylate-ethylene dimethacrylate) beads, paraffin, cetyl alcohol, phase change material, silica shell.

Nomenclature

AIBN	2,2'-Azobis(isobutyronitrile)
D_v	volume mean diameter
DSC	differential scanning calorimetry
EDMA	ethylene dimethacrylate
GMA	glycidyl methacrylate
M_w	molecular weight
PCM	phase change material
P(GMA-EDMA)	poly(glycidyl methacrylate-ethylene dimethacrylate) beads
P(GMA-EDMA)-CA-Me-SiO ₂	silica covered poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing cetyl alcohol

46	P(GMA-EDMA)-P-Me-SiO ₂	silica covered poly(glycidyl methacrylate-ethylene
47		dimethacrylate) beads containing paraffin
48	PVA	poly(vinyl alcohol)
49	PVP	poly(<i>N</i> -vinyl-2-pyrrolidone)
50	S_{BET}	specific surface area
51	TMMS	trimethoxy(methyl)silane
52	V_p	pore volume

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54 **1. Introduction**

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56 Thermal energy storage has received increasing attention during the past decades due to the
57 importance of energy saving. Latent heat storage is one of the most efficient ways of thermal
58 energy storing. The main benefits of latent heat storage compared with that of sensible heat are
59 the much higher storage density accompanying with a smaller temperature difference between
60 storing and releasing heat. Phase change materials (PCMs) are used for latent heat storage. Most
61 promising applications of PCMs are waste heat recovery, solar heating, building energy
62 conservation and air-conditioning systems. Most of the organic PCMs are non-corrosive and
63 chemically inert (stable), recyclable and compatible with numerous building materials. They have
64 desirable cohesion, a high latent heat per unit weight, low vapour pressure, no supercooling, and
65 offer congruent melting and self-nucleation. They have disadvantages such as low thermal
66 conductivities, flammability and high changes in volume during phase change. In order to
67 overcome these problems, their microencapsulation can be an efficient tool. Microencapsulation
68 is the entrapment of PCMs in natural or synthetic polymer capsules. The advantages of the
69 microencapsulated PCMs are their protection against the environmental effects, the enhancement
70 of specific heat-transfer area, and the elimination of the volume change of the PCM during phase
71 change by providing void space [1].

72 Most frequently applied microencapsulation techniques of organic PCMs are simple
73 coacervation, *in situ* polymerization of, e.g., methacrylates [1,2], other acrylic polymers [3] or
74 melamine–formaldehyde [4]. Emulsion methods/phase separation [5,6] and interfacial
75 coacervation and crosslinking [7] can be also efficient to prepare PCM-containing capsules of
76 core-shell structure.

Organic/inorganic composite form-stable phase change materials combine the advantages of the inorganic and the organic components [8,9]. The inorganic supporting material provides structural strength and prevents the leakage of the organic PCM component. Several preparation methods of the organic/inorganic composite form-stable phase change materials were described. The most important ones are absorption [8,10], solution intercalation [11] and sol–gel method [12,13]. Among them, the main benefit of the sol–gel method is the simplicity and low cost. In the present work, the form-stabilization of PCM was achieved by imbedding cetyl alcohol or paraffin in porous poly(glycidyl methacrylate-ethylene dimethacrylate) P(GMA-EDMA) beads, and the leakage of PCM was prevented by a silica shell prepared by sol-gel method. The carrier beads synthesized from this copolymer by suspension radical polymerization have not been used as support for PCMs so far. However, Chen et al. [14] covalently bound poly(glycidyl methacrylate) (PGMA) to poly(ethylene glycol) PCM through the ring-opening crosslinking reaction of oxirane groups in PGMA and end-carboxyl groups of poly(ethylene glycol). The main benefits of our prepared form-stable composite is that the porous organic beads provide shape-stable environment for the PCMs, and due to the capillary forces they are able to keep the latent heat storing material even in the liquid phase, while the inorganic silica shell inhibits the leakage that would definitely occur during long term application.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA; Aldrich; St. Louis, MO, USA) and ethylene dimethacrylate (EDMA; Ugilior S.A., France) were distilled before use under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN; recrystallized from ethanol), [(2-hydroxypropyl)methyl]cellulose (Methocel 90 HG), (2-hydroxyethyl)cellulose, poly(*N*-vinyl-2-pyrrolidone) K 90 (PVP; $M_w = 360,00$) and cetyl alcohol (CA) were obtained from Fluka (Buchs, Switzerland), poly(vinyl alcohol) (PVA; Polyviol W 25/140; $M_w = 80,000$) was from Wacker (Germany). Trimethoxy(methyl)silane (TMMS) and Tween 20 were from Sigma-Aldrich and paraffin (P), melting-solidification range 53-55 °C, from Paramo (Pardubice, Czech Republic). Other chemicals and solvents were purchased from Lachner (Neratovice, Czech Republic).

2.2. Synthesis of macroporous beads

Macroporous sorbents were prepared in a 10-l reactor equipped with anchor-type stirrer by the AIBN-initiated suspension radical polymerization of GMA and EDMA using an inert porogen [15]. Aqueous 0.2 wt.% PVP, 0.2 wt.% hydroxyethyl cellulose and 0.006 wt.% PVA solution (6 l) formed the continuous phase, while the dispersed phase consisted of GMA (480 g), EDMA (320 g), AIBN (4 g) and porogen. The porogen was composed of the mixture of toluene (885 g) and 1,2-dichloroethane (315 g) or that of cyclohexanol (1180 g) and dodecan-1-ol (20 g). While the polymerization employing the first mixture was used for production of large beads (~ 700 μm), the reaction using the second porogens yielded small beads (~ 150 μm) due to different stirring. The reaction mixture was stirred at 90 rpm (large beads) or 150 rpm (small beads) and heated to 75 °C for 6 h. The resulting beads were washed with water, toluene and methanol to remove porogens, unreacted compounds, and other soluble admixtures.

2.3. Loading of phase change materials in the beads and formation of silica shell

It is advantage that macroporous P(GMA-EDMA) beads are hydrophobic, which enables their wetting with PCM; as a result, the pores are well-filled with cetyl alcohol or paraffin avoiding thus need of vacuum degassing. Briefly, macroporous beads (2 g) were dispersed in molten cetyl alcohol (5 g) or paraffin (5 g) which were loaded at 65-100 °C. The PCM-loaded particles were separated by centrifugation using a stainless sieve to remove free cetyl alcohol or paraffin and again dispersed in aqueous 0.1 wt.% Methocel 90 HG solution (20 ml) at 70 °C in 50-ml reaction vessel under stirring with an anchor-type stirrer (500 rpm).

The silica shell was formed around the beads to keep PCM inside and to prevent particle aggregation at elevated temperatures. TMMS (1.36 g; 10 mmol) was thus hydrolyzed in 0.01 M HCl (0.54 g; 30 mmol) at room temperature to yield SiMe(OR)_3 hydrolysate. The volume of the mixture was adjusted to 5 ml by adding distilled water. The TMMS hydrolysate (1 ml) was added to the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change beads (P(GMA-EDMA)-PCM), the suspension was stirred at 70 °C for 3.5 h and the product eight times washed in 0.01 wt.% Tween 20 (100 ml each). Finally, the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change material-methyl silica particles (P(GMA-EDMA)-PCM-Me-SiO₂) were dried in air. The preparation of beads and the loading of PCMs as well as the formation of silica shell are drawn in Fig. 1.

2.4. Characterization methods

Carl Zeiss optical microscope (Germany) was used for the imaging of the particles. The size distribution of the beads was measured by Mastersizer 2000 (Malvern Instruments, Malvern, UK) applying laser diffraction method.

The specific surface area (S_{BET}) of the microspheres was determined by nitrogen adsorption (77 K) using a Gemini VII 2390 Analyzer (Micromeritics; Norcross, GA, USA). Pore volume was determined from cyclohexane or 1-chlorododecane regain using centrifugation method [16]. The PCM content of the beads was calculated after weighing 100 mg of the beads, and extracting the PCM 3 times from the microcapsules by each 5 ml n-hexane.

The thermal properties of the microcapsules compared to the neat PCMs were determined by a Setaram μ DSC3evo differential scanning microcalorimeter. The samples (10.2 mg cetyl alcohol, 12.8 mg paraffin, 17.6 mg of each of the microencapsulated PCM) were weighed into 100 μ l aluminium crucibles, and ethylene glycol as a heat transferring medium was added, which covered the microparticles, and then the system was closed by crimping a cap. The samples were cycled with a scanning rate of 0.6 $^{\circ}\text{C}/\text{min}$. The results were processed by the thermoanalyzer's Calisto Processing (v1.38) software. The corresponding melting/freezing enthalpies and onset temperatures were determined by the baseline integration method (Tangential sigmoid baseline type).

The covered beads were tested via accelerated thermal cycling in order to study whether they are capable to retain the PCM after several phase transition. One thermal cycling test included heating till the complete melting and cooling till the complete freezing of the phase change materials in the capsules. The tests were performed consecutively up to 1000 thermal cycles by heating and cooling using a Peltier element. DSC analysis was repeated after the thermal cycling using Setaram μ DSC3evo.

3. Results and Discussion

3.1. Porosity, size and PCM content

Macroporous sorbents were prepared by the AIBN-initiated suspension radical polymerization of GMA and EDMA. The mixture of toluene/1,2-dichloroethane and cyclohexanol/dodecan-1-ol was used as porogen. While the former materials were preferred for preparation of large particles,

the latter one was suitable for synthesis of small beads. Copolymerization of GMA (60 wt.%) with EDMA (40 wt.%) produced particles possessing reactive oxirane groups. Two types of beads were thus obtained: large P(GMA-EDMA)L and small P(GMA-EDMA)S microspheres. Both of these beads had moderate specific surface area and pore volume, and these properties did not show significant differences (Table 1).

The P(GMA-EDMA) beads were rather hydrophobic, i.e., compatible (well-wettable) with the PCMs, which facilitated their fast imbibition, filling of the pores and air displacement thanks to the low interfacial tension. The large and the small beads were filled with paraffin and cetyl alcohol PCMs, respectively. After PCM loading, the particles were dispersed in the [(2-hydroxypropyl)methyl]cellulose solution and via hydrolysis and condensation of silane, a shell of silica was formed in sol-gel process using TMMS hydrolysate. Both large and small microcapsules had regular spherical shape (Fig. 2).

The large particles loaded with paraffin PCM and covered by silica were 300-1400 μm in size (average size: 643 μm), while the small beads with cetyl alcohol and silica shell ranged between 70 and 200 μm (average size: 111 μm) (Fig. 3, Table 2).

Although the specific surface area and the pore volume of large and small beads were very similar (Table 1), the PCM content of the small beads was substantially higher than that of the large beads (Table 2). The reason for this finding must be that the cetyl alcohol-copolymer interaction is more favourable than the adsorption of paraffin to the carrier of the same composition.

3.2. DSC analysis

Thermal properties of the PCM-containing composites were studied by DSC measurements. The thermal energy storage capacities of pure paraffin and P(GMA-EDMA)-P-Me-SiO₂ are compared in Fig. 4a. The melting and crystallizing enthalpies of the P(GMA-EDMA)-P-Me-SiO₂ composite were found to be 78.0 J/g and 78.8 J/g, respectively, which was slightly lower than the calculated values according to paraffin content (42.9 wt.%). This difference might be explained by the thermal isolating effect of the silica shell. The melting and solidifying latent heats of P(GMA-EDMA)-CA-Me-SiO₂ microcapsules were 96.1 J/g and 94.5 J/g (Fig. 4b), respectively. These values were a bit lower again related to the ones which can be determined from their PCM

content (48.9 wt.%). The latent heat storage capacity of our developed composites is higher than the form-stabilized PCMs that were prepared from similar types of carriers or with similar procedures. E.g., the thermal energy storage capacity of poly(ethylene glycol) PCM crosslinked with PGMA was around 70 J/g [14]. Microencapsulated palmitic acid with titanium dioxide shell as shape-stabilized thermal energy storage material was formed through a sol-gel process. The microcapsules melted and solidified with latent heat of 63.3 J/g and 47.1 J/g, respectively [17].

3.3. Thermal reliability

If one would like to use PCM-containing microcapsules for latent heat storage, leakage must be avoided during the phase change. To analyze the potential leakage, the capsules were 1000 times heated and subsequently cooled. The heat storage capacity of the PCM-containing capsules was investigated by DSC before and after the thermal cycles. It was assumed that if the heat capacity of microcapsules did not change after the thermal cycling test, the PCM did not leak from the composites. In case of leakage significant decrease of heat capacity could be observed. In contrast, the melting and crystallizing enthalpies of cetyl alcohol (Fig. 5b) containing composites decreased only slightly after 1000 heating-cooling cycles, although the heat storage capacity reduction of silica-covered paraffin-containing beads was not negligible (Fig. 5a). This result verifies that the cetyl alcohol adsorption is stronger to the copolymer than that of the paraffin, and the leakage of latter PCM may be higher than acceptable for real use.

4. Conclusions

Large and small macroporous poly(glycidyl methacrylate-ethylene dimethacrylate) beads were synthesized by the suspension polymerization technique and imbibed with high amounts of paraffin and cetyl alcohol phase change materials. The PCM-loaded beads were coated with a protective shell of silica via sol-gel synthesis using trimethoxy(methyl)silane hydrolysate. According to the results obtained by differential scanning calorimetry, both composites showed high latent heat storage capacity. Due to the higher cetyl alcohol content, which was the result of its higher affinity to the carrier copolymer, larger melting and solidifying enthalpies were measured in cetyl alcohol containing beads coated by silica compared to those values found for similar composites but with paraffin phase change material. The beneficial latent heat storage

capability of the former beads could be preserved more effectively after the thermal cycling tests. Nevertheless, it should be emphasized that the used quick thermal cycling test is not appropriate to model the reliability of the microspheres in long-term (during years) application. In order to study long-term performance, investigations under longer stress would be useful, which can be suitable to simulate the real use.

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290 Figure captions:

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292 Fig. 1 Preparation process of the beads

293 Fig. 2 Optical micrographs of P(GMA-EDMA) beads containing paraffin (A) and cetyl alcohol
294 (B) covered by silica. Squares indicate size of 0.5 mm x 0.5 mm.

295 Fig. 3 Size distribution of cetyl alcohol- (P(GMA-EDMA)-CA) and paraffin loaded (P(GMA-
296 EDMA)-P) microspheres. Squares indicate size of 0.5x0.5 mm.

297 Fig. 4 DSC of paraffin and P(GMA-EDMA)-P-Me-SiO₂ (A), as well as cetyl alcohol and
298 P(GMA-EDMA)-CA-Me-SiO₂ beads (B).

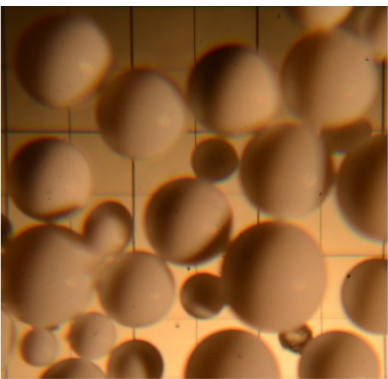
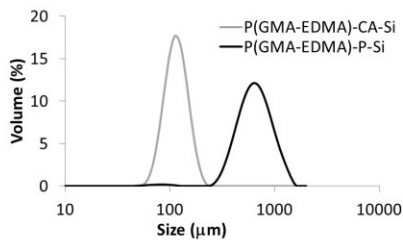
299 Fig. 5 DSC of beads containing paraffin (marked with P) (A) or cetyl alcohol (marked with CA)
300 before (P(GMA-EDMA)-P/CA-Me-SiO₂) and after (P(GMA-EDMA)-P/CA-Me-SiO₂-1000c)
301 1000 heating-cooling cycles.

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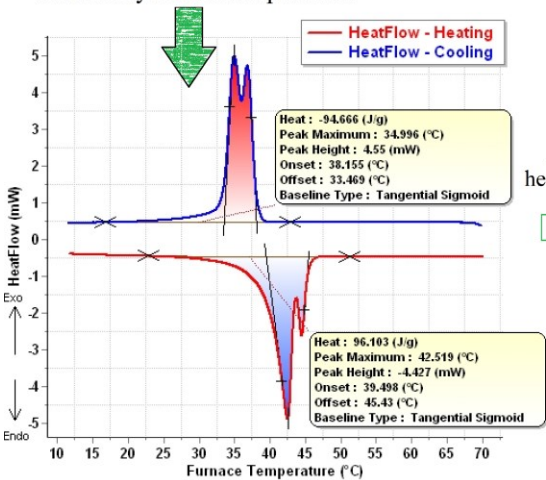
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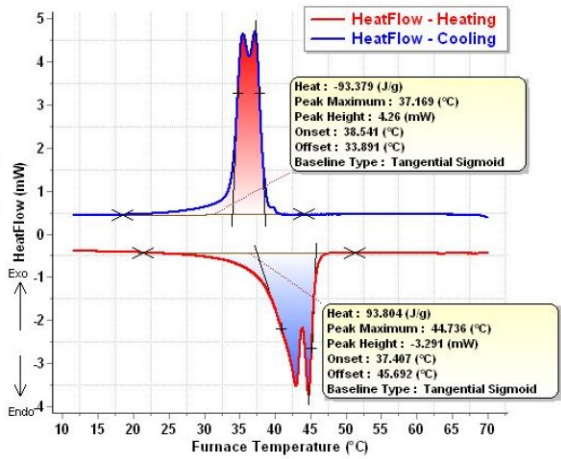
Small beads filled with cetyl alcohol covered by silica nanoparticles



Large beads filled with paraffin covered by silica nanoparticles



After 1000 heating-cooling

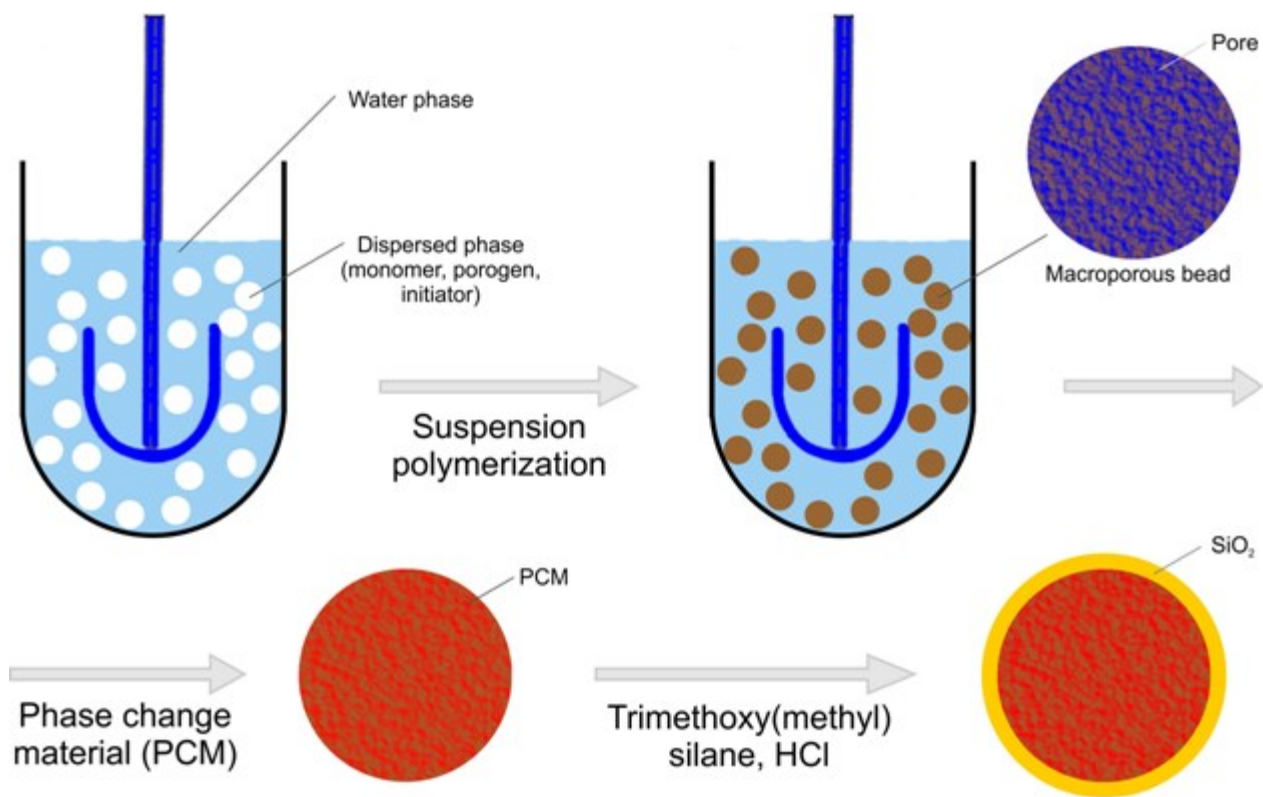


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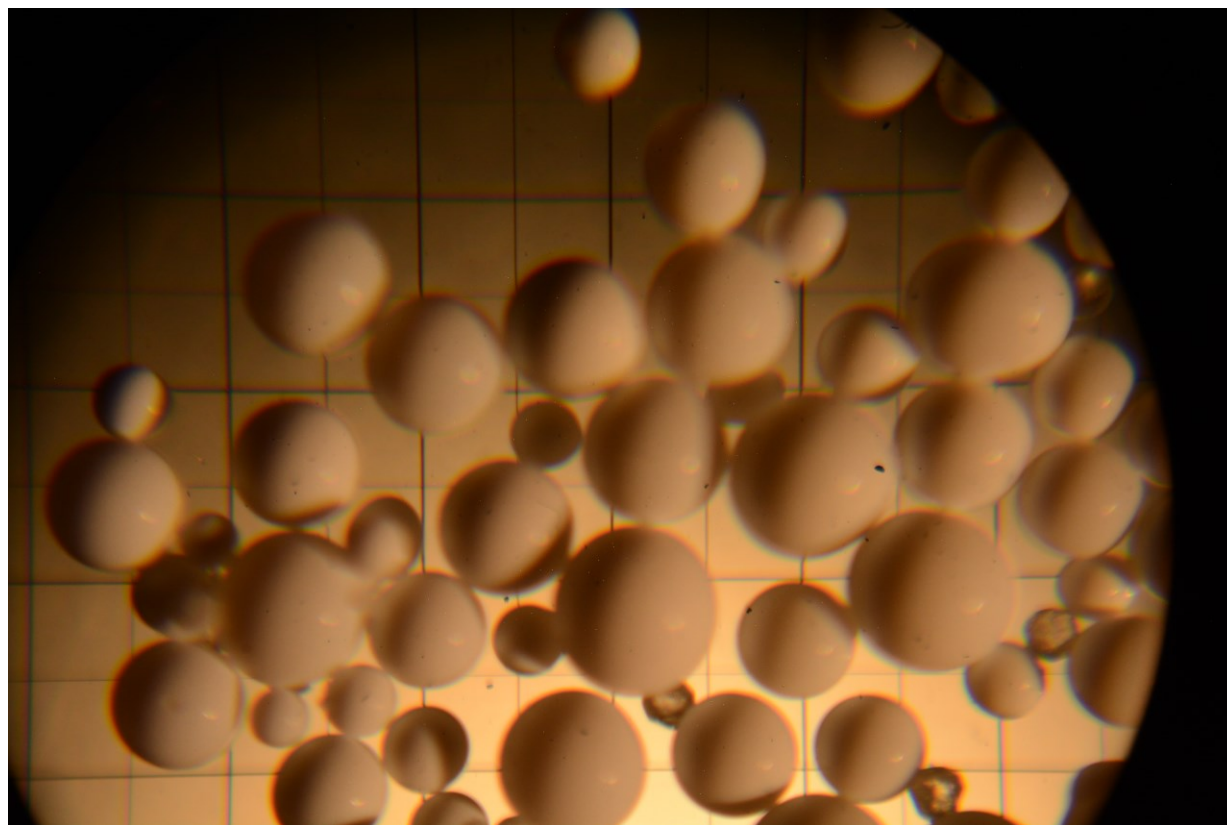
308 Fig 1



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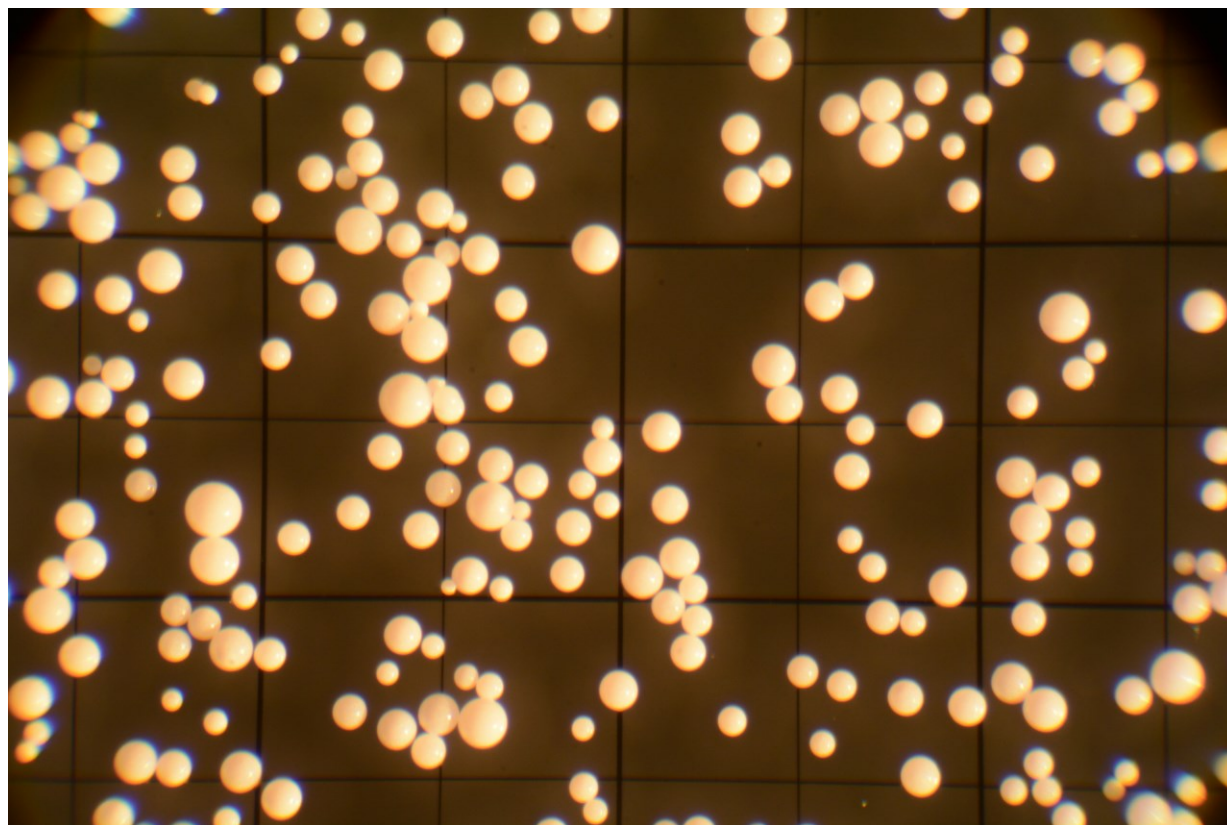
311 Fig2a



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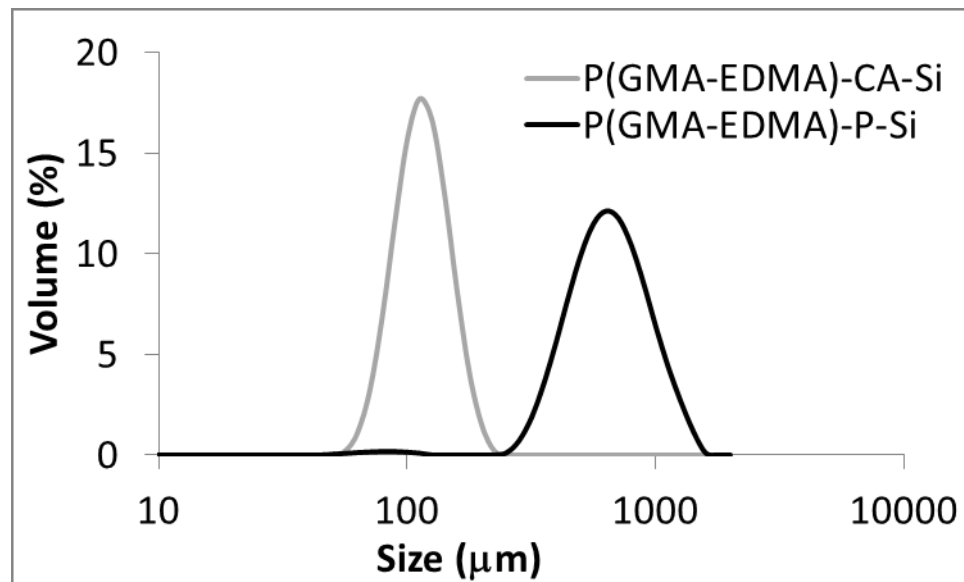
314 Fig2b



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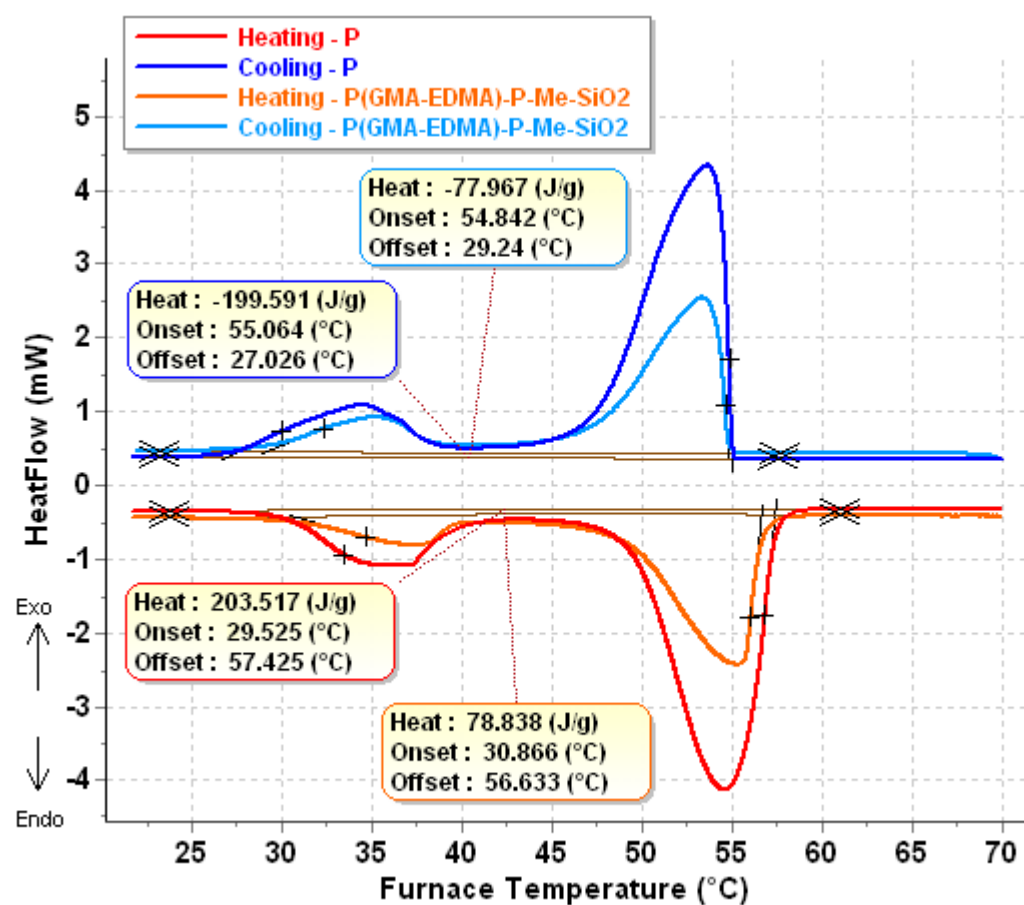
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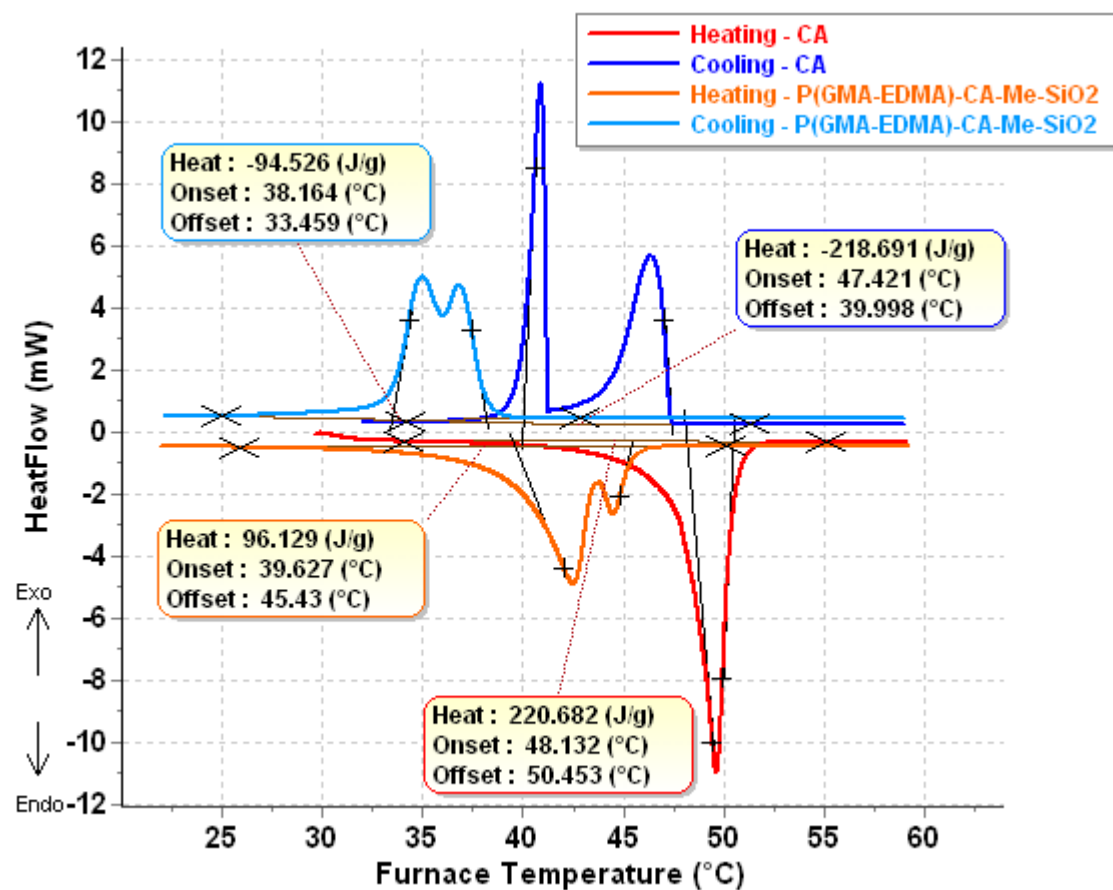
320 Fig4a



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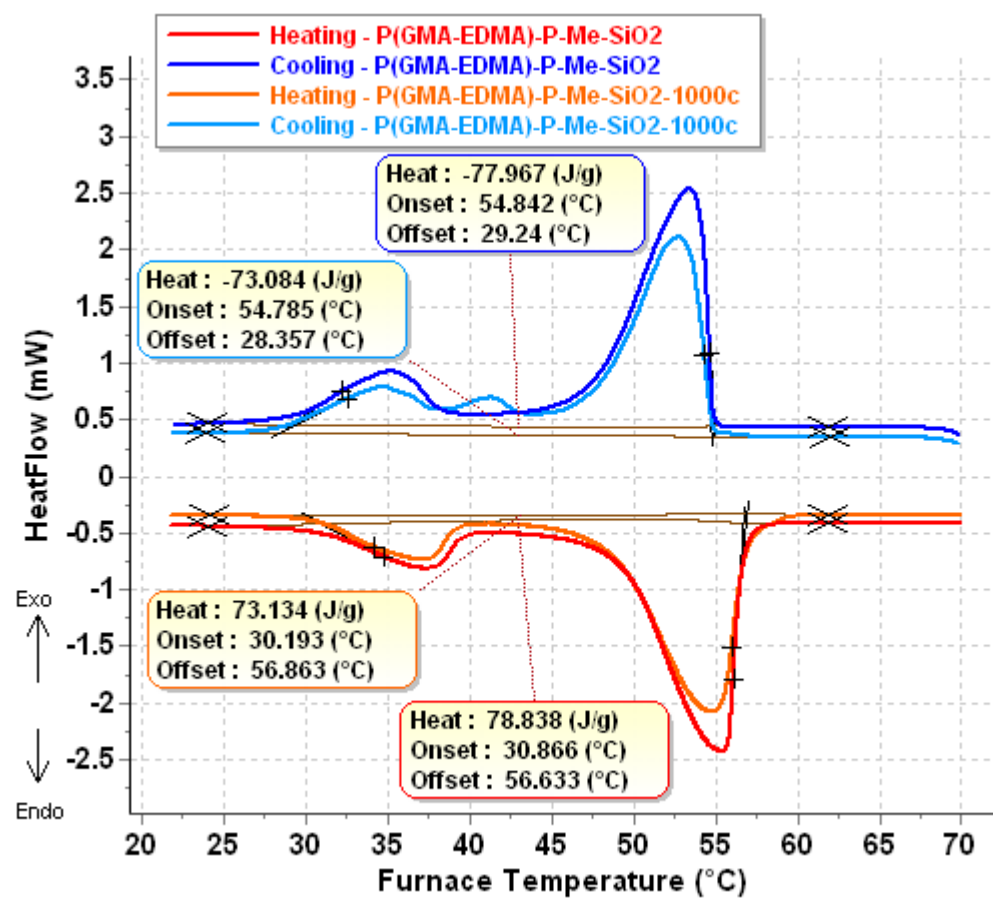
323 Fig4b



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326 Fig5a



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